PATENT SPECIFICATION

(11) 1226876

DRAWINGS ATTACHED

(21) Application No. 15654/68 (22) Filed 1 April 1968
(31) Convention Application No. 20619 (32) Filed 1 April 1967 in
(33) Japan (JA)
(45) Complete Specification published 31 March 1971
(51) International Classification C 01 g 49/06
(52) Index at acceptance
C1A N13A
H1H 2 3C 3E 3F 5C2

(54) PROCESS FOR PRODUCING HIGHLY PURE FeOOH POWDER

(71) We, NIPPON ELECTRIC COMPANY, LIMITED, a Company duly organized and existing under the laws of Japan and having its executive office at 7—15, Shiba Gochome, Minato-ku, Tokyo-to, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods for producing highly pure and stoichiometric FeOOH particles; to iron oxyhydroxide powder produced by such methods, and to ferrites incorporating such powder.

The object of this invention is to provide a method of manufacturing iron oxyhydroxide or iron oxide on a large scale economically and efficiently which has excellent properties as a raw material for manganese-zinc ferrites.

Recently, the quality requirements for ferrites are becoming increasingly higher in the field of electronic apparatus, and raw materials of extremely high purity are sought for the production of such ferrites. The presence of more than 0.05% of an alkali metal, an alkaline earth metal, or SiO_2 in the raw materials such as iron oxide, manganese oxide, and zinc oxide makes it impossible to manufacture from such raw materials a manganese-zinc ferrite whose μ_o at 100KC is more than 2000 and $\tan\delta/\mu_o \times 10^6$ is less than 2. Since iron oxide is the main component of the ferrites among the oxide raw materials, impurities in the iron oxide have a fatal effect on the quality of the ferrites.

The raw material, iron oxide, is mostly obtained by roasting in air at a temperature above 660°C iron sulphate ($FeSO_4.7H_2O$) recovered from a waste pickling liquor in the steel-making industry or iron sulphate produced as a by-product in the manufacture of titanium dioxide. In these cases, CaO and SiO_2 may enter from the vessel or from the air during the roasting process or from water during water washing and it is almost impossible to keep those contaminants below 0.1%. In some sector of the industry, there is practiced another method. In that method, NaOH is added to an aqueous solution containing a ferrous salt, air is passed through the solution to effect the oxidation and to produce α-FeOOH in a fine needle form, and then the solution is subjected to oxidation for 100—200 hours, with iron scraps immersed therein, to produce α-FeOOH which is to be used as the raw material. This method shall be called the "wet method" hereinafter. In this method, it is extremely difficult to reduce the amount of alkali ions (Na) below 0.05%. On the other hand, the thermal decomposition of either iron carbonyl or highly pure iron oxalate is adopted as a means of obtaining pure iron oxide, but this process involves many industrial difficulties.

Against this state of art, the present inventors proposed a process in which highly pure iron powders such as crushed electrolytic iron were transformed to highly pure hydrated iron oxide by the wet method and said oxide was used in the manufacture of high-quality manganese-zinc ferrites.

The present inventors further carried out extensive and systematic experiments on the foregoing method and evolved a method for producing efficiently and economically on a large scale FeOOH powders which have unproved properties as a raw material for high-quality manganese-zinc ferrites. According to this prior method of the present inventors, it was possible to produce hydrated iron oxide (mainly α-FeOOH) containing less than 0.1% by weight each of alkali, alkaline earth metal, and SiO_2.

The present invention is based on the finding that α- and γ-FeOOH precipitate particles can be well grown only by oxidizing a ferrous solution having pH value of 3.0 or more without the intermediate precipitation of so-called

"green rust" whose crystal structure is of the layer lattice type containing Fe^{+2} and Fe^{+3}.

Further aspects relate to the products of such methods, and to ferrites made therewith.

FeOOH precipitates of a particular shape, not obtainable by any other methods are thus obtained. A further study of the above-mentioned reaction system led to the following preferred method of this invention.

Into a reaction vessel containing an aqueous solution of an acid having a pH of 3 or more, and free of alkali, is added iron powder, and an oxygen-containing gas such as air is forced into the solution from the bottom of the reaction vessel to agitate the solution. The oxidation of the aqueous solution proceeds while the iron powder is suspended and well dispersed, and precipitates containing Fe^{+3} ions are formed. The iron powder gradually dissolves as Fe^{+2} ions and the latter are oxidized to form precipitates. The formation of precipitates lasts until the iron powder disappears completely. The kinds of precipitates containing ferric ions vary depending upon the reaction conditions in this reaction system, the major kinds being α-FeOOH, γ-FeOOH, Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3. The main reaction conditions affecting the kinds of precipitates are as follows:

(i) Temperature of the solution;
(ii) The particle size, amount, and surface area, of the iron powder dispersed in the solution;
(iii) Kinds of anion present in the solution and their concentration; and
(iv) The pH of the solution.

The present inventors have examined the relation between the above-mentioned conditions and the kinds of precipitates, and have also studied the manganese-zinc ferrites obtained when those different precipitates are used as raw materials. As a result, they found conditions necessary for obtaining highly pure FeOOH consisting of the particles of a desired size. Furthermore, from the standpoint of production efficiency and cost, the following factors were considered in addition to the above four conditions.

(v) Method of blowing air and the feed rate.
(vi) Reaction time.

The preferred method of this invention comprises the steps of adding highly pure iron powder whose particle size is not more than 140 microns, to an aqueous solution of one or more of the following acids; sulphuric acid, hydrochloric acid, nitric acid, and acetic acid; in a concentration ranging from 0.12 to 0.25 M, to an extent that the surface area of said iron powder is not less than 0.3 m^2 per litre of said solution (the amount of iron powder of particle size 40 microns or less should be not more than 25 gram per litre of said solution), and blowing a gas containing oxygen, such as air, into said solution while keeping said solution at a temperature of 50 to 70°C to cause the oxidation reaction under the condition that said iron powder is suspended and sufficiently dispersed in said solution, whereby a highly pure FeOOH powder is obtained which consists of FeOOH particles of a few microns in length, 0.3 micron or more in width, and 0.1 micron or more in thickness, and which contains 88.2 to 88.7% of Fe_2O_3 and not more than 0.1% of acid radicals.

If care is exercised so that the starting materials, water, and air are purified and also contaminations due to impurities from the reaction vessel and dust in the atmosphere are avoided, it is possible to obtain highly pure and efficient FeOOH powder in which the impurities which adversely affect high-quality manganese-zinc ferrites such as alkali metals, alkaline earth metals, and SiO_2 are below the allowable limit.

The present inventors have thus succeeded in making excellent FeOOH powder which not only satisfies the requirement on impurities, but also possesses the four features 1)-4) described below.

1) All the powders obtained by the method of the present invention are composed of FeOOH, in which the iron content is high and the fluctuations in iron content are negligible.

In the known wet method, the particle diameter of the resultant α-FeOOH powders is small, and consequently an absorption of H_2O and SO_4^{-2} takes place to a large extent and the Fe_2O_3 content generally fluctuates between 84 and 87%.

Also in a method previously proposed by the Inventors, α-Fe_2O_3, Fe_3O_4, etc. may be present in the range of 1—20%, depending on the reaction conditions, and in such cases the Fe_2O_3 content in the powder may fluctuate considerably.

The fluctuation of the ratio of Fe_2O_3: MnO:ZnO affects the ferrite properties markedly in high-quality manganese-zinc ferrites, and the allowable fluctation of Fe_2O_3 is only 0.1%. Consequently, in the manufacture of such ferrites, the weighing of the raw material Fe_2O_3 should be done carefully and with precision, and it is required that the fluctuation of the Fe_2O_3 content in the raw material should be made as small as possible. In the method of this invention, the reaction conditions are such that the resultant powder consists only of α-FeOOH particles or γ-FeOOH particles or a mixture thereof (not comprising α-Fe_2O_3 or Fe_3O_4), and simultaneously the amount of a sorbed water is minimized by making the precipitated particles large. Accordingly, the chemical component of the powder prepared by the method of this invention is FeOOH, and the Fe_2O_3 content contained therein fluctuates only in the range of 88.2—88.7% which is near the theoretical

value of 88.9%, the remainder being H_2O a sorbed.

2) The powders obtained by the present invention contain practically no detrimental acid radicals. In another method previously proposed by the Inventors, for example, for the preparation of hydrated iron oxide from a sulphuric acid solution, more than 1.0% of SO_4 was present depending upon the reaction conditions.

In the presence of such acid radicals, not only the miscibility with other oxides is poor, but also noxious gases may be generated and furnaces and vessels are corroded during heating for ferrite formation. Consequently, it is necessary to remove acid radicals as much as possible. The present inventors found the following causes for the presence of acid radicals: that when the precipitate particles are fine, the separation of the particles from the mother liquor and the washing thereof is difficult and hence the content of acid radicals in the powder is relatively high; that particularly when the precipitates of α-Fe_2O_3 and the spinel type Fe_3O_4 are formed, they are generally of very fine particles of less than 0.1μ and ordinarily contain acid radicals; and that a removal of acid radicals is difficult when α-FeOOH or γ-FeOOH is fine. Particles produced by the present inventors whose dimensions are; a few microns in length, more than 0.3μ in width, and more than 0.1μ in thickness; are easy to wash with water thus reducing the content of acid radicals in the formed powder below 0.1. Since the conventional wet method employs alkali, precipitates having the formula $RFe_3(SO_4)_2(OH)_6$ (R=Na, K, or NH_4) which are insoluble may be formed and contamination with them is inevitable. In the method of this invention, however, such salts are not formed.

3) The powder of γ-FeOOH also possesses excellent properties as a raw material for ferrites. A method proposed by the Inventors was concerned with obtaining the α-FeOOH powder alone, but study by the present inventors has indicated that the γ-FeOOH powder not only satisfies the requirements (1) and (2) mentioned above, but also has excellent properties as a raw material for the production of manganese-zinc ferrites. The particles of γ-FeOOH are shaped like a thin plate and are readily ground and mixed in a ball mill. They also have the advantage of being transformed to γ-Fe_2O_3 by thermal decomposition, then further to α-Fe_2O_3 on heating, with a resultant high rate of ferrite formation. The method of this invention provides raction conditions under which the γ-FeOOH powder alone or a mixture thereof with α-FeOOH is produced.

4) The shape of the particles produced is remarkable, as compared with that of the conventional methods. The particles of α-FeOOH and γ-FeOOH respectively prepared by the conventional wet method are in the order of $1\mu \times 0.1\mu$ in size, as shown in A, B, and C of Figs. 4 and 5 described below. On the other hand, the α-FeOOH or γ-FeOOH particles prepared by the method of this invention are of relatively large plate shape, which is a few microns in length, more than 0.3μ in width, and more than 0.1μ in thickness, as shown in Fig. 4D and Fig. 5D. As a result, in addition to the advantage of (2), they show a higher apparent density than that of the conventional particles because of a smaller ratio of length to width and a larger thickness, and they can be ground very quickly in a ball mill because of their thin plate shape, and can be mixed readily with oxides of manganese and zinc.

The powders produced by the method of this invention thus have excellent properties. Moreover, from the points of view of large-scale production and reduction of production cost, this invention is excellent as the rate of formation of the FeOOH particles is more than 10 times as fast as that of the known wet method. Even in the reaction system previously proposed by the Inventors in which iron oxide precipitates (α-Fe_2O_3, Fe_3O_4) are formed instead of FeO.OH, the rate of formation was slower.

The invention will be clearly understood from the following description of certain methods and products embodying the invention with reference to the accompanying drawings in which:—

Fig. 1 shows the relation between the oxidation time of an H_2SO_4 aqueous solution containing the iron powder and the amount of the FeOOH powder obtained.

Fig. 2 shows the relation between the feed rate of air into an HNO_3 aqueous solution containing the iron powder and the amount of the FeOOH powder obtained.

Fig. 3 shows the relation between the concentration of SO_4^{-2} in an H_2SO_4 aqueous solution containing the iron powder and the amount of the FeOOH powder obtained.

Fig. 4 gives electron micrographs of the α-FeOOH particles.

Fig. 5 gives electron micrographs of the γ-FeOOH particles.

Fig. 6 shows the relation between the thermal decomposition heating temperature of FeOOH particles and the particle diameter of α-Fe_2O_3 formed.

Item (1)

Conditions for obtaining precipitates composed of FeOOH alone:

In the reaction system described above α-Fe_2O_3 and spinel type iron oxides (γ-Fe_2O_3 or Fe_3O_4) may be formed (in addition to α-FeOOH, γ-FeOOH, and a mixture thereof, depending upon the reaction conditions), and contaminate the FeOOH precipitates.

α-Fe_2O_3 will be formed when the reaction

temperature stays above 70°C, where any one of HNO_3, HCl, CH_3COOH is used as an acid.

When any one of HCl, HNO_3, etc. is used, the formation of spinel type iron oxides (γ-Fe_2O_3, Fe_3O_4) is observed over 70°C and also even below 70°C when more than 25 g. or iron powder whose particle diameter is 40μ or less is added to 1 litre of the aqueous solution of the acid.

It has also been found that spinel type iron oxides are formed when the concentration of the acid used is below 0.01M.

Accordingly, for the purpose of obtaining precipitates composed of FeOOH alone, it is necessary to maintain the reaction temperature at 70°C or less to keep the acid concentration at least 0.01M and to prevent the amount of iron powder of 40μ or less in particle size from going over 25 g. per litre of the reaction solution.

Item (2)

Conditions for obtaining FeOOH of large particle size and small dimensional anisotropy:

As described, above, the large particle size is not only favourable for easy filtration and water washing of the precipitates, but also indispensable for reducing the absorption of harmful acid radicals and water to produce highly pure FeOOH powder with small fluctuation in the Fe_2O_3 content. At the same time, the particles having large particle size and small dimensional anisotropy can be ground and mixed with efficiency and are advantageous for the production of high-quality manganese-zinc ferrites. The conditions for obtaining such particles are as follows:

(i) In general, the higher the reaction temperature the larger the particles become. Below 50°C, it is difficult to obtain the particles of useful size as mentioned above, even if, any other conditions are altered. Consequently, it is necessary to keep the reaction temperature at 50°C or above.

(ii) Concentration of the acid affects the growth of particles, and generally speaking, the higher the acid concentration, the larger the particles grow. It is desirable to use an acid concentration of more than 0.1M to obtain particles of the above-mentioned useful size.

The particles prepared by the conventional wet method using alkalis are shaped like fine needles which are less than 1.2μ in length, less than 0.2μ in width, and less than 0.1μ in thickness. On the other hand, if the above-mentioned conditions (i) and (ii) are satisfied using the present method, particles are obtained which are more than a few microns in length, more than 0.3μ in width, and more than 0.1μ in thickness: that is, in which the ratio of length to width is small or the dimensional anisotropy is small.

The following example incorporates the foregoing conditions.

Example 1

To 1 litre of 0.25M-H_2SO_4 was added 51.7 g. of crushed electrolytic iron powder of less than 140μ. The solution containing the iron powder was maintained at 70°C. and air was bubbled into the solution at the rate of 650 litres/hr, while the iron particles were maintained uniformly dispersed in the solution, and oxidation was performed. After a period of 8 hours, the iron powder was completely dissolved and yellowish brown non-ferromagnetic precipitates were formed. The precipitates were filtered off, washed with water, and dried at about 110°C, to obtain samples of powder form. The analytical results of the powder are shown in Table 5.

Table 1

X-ray analysis	Yield	Chemical analysis			Particle size in μ
		Fe_2O_3	SO_4	H_2O	
mixture of α- and γ-FeOOH particles	36.5 g	88.22%	0.07%	0.08%	Length : 5—10 Width : 0.3—0.8 Thickness : 0.1—0.2

Item (3)

Conditions for producing FeOOH precipitates with efficiency:

The range of conditions for precipitating FeOOH without contamination of α-Fe_2O_3 and spinel type iron oxides is clear from the foregoing Item (1). However, even in this range, the rate of formation of precipitates varies considerably depending upon the factors such as the amount of iron powder added, the concentration of acid, and the feed rate of air, and affects the production efficiency and cost if the FeOOH powder is to be made on a large scale. The present inventors made a study on these factors and found the optimum conditions to be as described in (i) to (iii) below.

(i) Effects of the amount of addition and the particle size of iron powder on the rate of formation of FeOOH.

Below pH 6 the rate of formation of

FeOOH becomes higher (I) as the surface area of iron powder per unit volume of the aqueous acid solution becomes larger which is caused either by reduction in particle size of the iron powder, or by increase in the amount of the powder, and (II) as the amount of iron powder dissolving into the acid solution in unit time becomes larger. However, if the feed rate of air is reduced and the amount of dissolved oxygen becomes insufficient for oxidation of Fe^{+2}, the feed rate of air becomes the rate-determining factor.

On the other hand, supposing the feed rate of air is sufficiently high, the rate of dissolution becomes the rate-determining factor if the particle size of iron is large and the rate of dissolution becomes low. This phenomenon will be illustrated by the following example.

EXAMPLE 2

To 1 litre of a 0.21M H_2SO_4 solution was added 31.5 g. of crushed electrolytic iron powder of less than 140μ with the particle distribution as shown in Table 2, and the oxidation was carried out by keeping the temperature of the solution at 70°C and passing clean air at a rate of 650 litres/hr while maintaining the iron particles uniformly dispersed in the solution at all times. Yellowish brown non-ferromagnetic precipitates formed, were filtered respectively 2, 5, 8, and 10 hours after the start of the reaction, washed with water, and subjected to a chemical analysis. Thus, the Fe_2O_3 content was determined and the amount of FeOOH formed was calculated. The results are represented by Curve A in Fig. 1.

TABLE 2

Particle size (μ)	140—104	104—74	74—61	61—43	43 and below
Weight %	1.0	8.4	10.4	15.8	64.4

Curve B in Fig. 1 indicates the results obtained when the amount of iron powder was made 20 g. under conditions otherwise identical to the above.

Curve C in Fig. 1 shows the case where 40 g. of crushed electrolytic iron powder of 200—280μ was added to 1 litre of 0.21M H_2SO_4, the solution was kept at 65°C, and air was passed at a rate of 1500 l/hr.

As is apparent from Fig. 1, the rate of formation of FeOOH differs remarkably depending on whether the particle diameter of iron is less than 140μ or in the range of 200—280μ. In the former case, the iron powder completely dissolves in 6—8 hours at the feed rate of air of 650 l/hr and is converted to the FeOOH precipitates, whereas in the latter only about 1/4 of the iron powder was dissolved in 10 hours at the feed rate of air of 1500 l/hr and precipitated as FeOOH. It appears that a larger particle diameter of iron powder led to a lower rate of the dissolution of iron.

The present inventors conclude that it is desirable to use the iron powder of not more than 140μ in such an amount as to obtain a surface area of at least 0.3 m^2 per 1 litre of the aqueous solution for the efficient production of the FeOOH precipitates.

(ii) Effect of the feed rate of air on the rate of formation of FeOOH.

The following example was carried out to study this effect.

EXAMPLE 3

To 1 litre of 0.25M-HNO_3 in a cylindrical reactor of 8 cm diameter (about 50 cm^2) was added 100 g. of crushed electrolytic iron powder of 140—100μ and while keeping the temperature of the solution at 55°C, air was introduced from the bottom of the reactor for 6 hours at various rates. After the reaction was over, the unreacted iron powder was removed from the mixture of FeOOH precipitates and iron powder. The relation between the amount of FeOOH thus obtained and the feed rate of air is shown in Fig. 2. It is seen that the rate of formation is independent of the feed rate below 600 litres/hr, but increases rapidly above 600 litres/hr. This is because iron powder of 100 to 140μ moves up from the bottom and become uniformly dispersed in the solution at a feed rate of 600 l/hr or more. However, at a feed rate of 1500 l/hr or more, the rate of formation no longer increases but the increased flow of air causes the temperature of the solution to fall.

As the particle size of iron powder becomes smaller, the feed rate of air necessary to disperse the iron powder becomes lower. A feed rate of 600 l/hr per 50 cm^2 of the sectional area of the reactor is preferable, and a series of experiments have indicated that a range of 600—1500 l/hr/50 cm^2 is most suited for the efficient production of the FeOOH powder.

(iii) Effect of the concentration of acid radicals on the rate of formation of FeOOH.

The following example was carried out to examine this effect.

EXAMPLE 4

To 1 litre of an aqueous H_2SO_4 solution of various concentrations was added 31.7 g. of the crushed electrolytic iron powder of less

than 140 μ having the particle distribution shown in Table 2, and while keeping the solution at 70°C, clean air was introduced at a rate of 650 l/hr for 6 hours to maintain the iron powder uniformly dispersed in the solution and to effect the oxidation. The relation between the amount of FeOOH formed and the concentration of H_2SO_4 is shown in Fig. 3. It is apparent from Fig. 3 that the rate of formation of FeOOH is high at a H_2SO_4 concentration of 0.12M or more. However, at concentrations above 0.25M, the amount of the formed FeOOH decreases due to an increase in the amount of dissolved Fe ions, although the rate of formulation is not appreciably affected.

The above and other results show that the optimum acid concentration is in the range of 0.12—0.25M. It was also observed that the preferable concentration range is also 0.12—0.25M for acids other than H_2SO_4.

By means of the methods described above, very pure FeOOH powder can be produced efficiently and economically. The advantages thereby obtained are as follows:

1) All the powder is composed of FeOOH; preferably γ-FeOOH powder; and the iron content is high and practically not fluctuating.

2) The powder contains nearly no harmful acid radicals.

3) FeOOH powder, and particularly γ-FeOOH powder, has properties suitable as a raw material for the production of ferrites.

4) The particle shape is suited for the production of ferrites. The optimum temperature of the acidic solution is 60—70°C in case H_2SO_4 is used, and 50—60°C in case HCl, HNO_3, or CH_3COOH is employed. The reason is that in the former temperature range the rate of formation of FeOOH is high and the particle size is large and in the latter a contamination of undesirable oxides does not occur in addition to the higher rate of formation of FeOOH.

The products to be obtained by heating the pure FeOOH particles obtained by the above methods will now be described.

When heated at temperature above 250—270°C, the FeOOH particles give Fe_2O_3 due to dehydration.

The γ-FeOOH particles are dehydrated to fine particles of γ-Fe_2O_3, but at a temperature above 350°C they are readily transformed into α-Fe_2O_3 and grow. The α-FeOOH particles, upon heating, change to α-Fe_2O_3 particles whose size corresponds to the temperature of heating.

Fig. 6 shows the relation between the particle diameter and heating temperature. This is the result obtained by heating the α-FeOOH particle of 2—5μ in length, 0.5—1.0μ in width, and more than 0.1μ in thickness for 2 hours at a given temperature to produce α-Fe_2O_3 particles and by calculating the particle diameter of the α-Fe_2O_3 particles from the specific surface area by the B.E.T. method assuming that the particles are spherical. When the dehydrated products of the pure FeOOH produced by the above methods are to be used as raw material for ferrites, it is preferable to dehydrate at a temperature of 550°C or less. Bu such a heat treatment, Fe_2O_3 particles of less than 0.05μ are obtained.

Description will now be given of the production of ferrite material, including alternative processes for the production of FeOOH powder, and a process for producing the ferrite from materials including such FeOOH powder.

EXAMPLE 5

To 60 litres of 0.25M aqueous solution of acetic acid was added 1.00 kg of crushed electrolytic iron powder containing 0.001 wt% of Mn, 0.002 wt% of Si, and 0.001 wt% of C, based on Fe and having the particle size distribution shown in Table 2. Air purified by concentrated KOH and water was passed through the solution kept at 50°C at a rate of 4.2 m^3/hr for 1 hour, and then at 55°C for 9 hours at a rate of 4.2 m^3/hr. At the end of this period, the iron particles disappeared almost completely and orange non-ferromagnetic precipitates were formed. The solution containing the precipitates was filtered, and the precipitates were washed with water and dried at 105°C to give 1.5 kg of mobile orange non-ferromagnetic powder. An X-ray analysis indicated the crystal structure of γ-FeOOH; and that a chemical analysis showed that the Fe_2O_3 content was 88.7% and that 0.004% of Si and less than 0.002% of other metal ions were present. The particles were 1—2μ in length and about 0.12μ in thickness, and the tapping density was 1.02.

EXAMPLE 6

To 70 litres of 0.15M H_2SO_4 solution was added 1.5 kg of the same iron powder as in Example 5, and while keeping the temperature of the solution at 68°C, clean air was introduced at a rate of 4.5 m^3/hr for 4 hours. Thereafter, 0.5 kg of the same iron powder was further added, and the oxidation was continued for 5 hours. The iron powder almost disappeared and yellowish brown precipitates were formed. The mother liquor was decanted off and the precipitates were washed with water by decantation, filtered, and dried at 150°C to give about 3 kg of yellowish brown non-ferromagnetic powder. The powder showed the crystal structure of α FeOOH, and contained 88.4% of Fe_2O_3 and 0.018% of SO_3 according to a chemical analysis. As impurities, 0.005% of Si and less than 0.002% of other metal irons were found. The particles were 0.5—1.0μ in width and 2—3μ in length, and the tapping density was 0.97.

The Fe_2O_3 contents in the FeOOH powders in Examples 5 and 6 are closer to the theoretical value (88.9%) than those obtained by the conventional method. This is probably by the

reason that the particle size by this method is larger, resulting in a reduction of adsorbed matters; and that the particles do not contain insoluble salts of the formula

$$RFe_3(SO_4)_2(OH)_6$$

(R represents K, Na, NH_4), since the FeOOH particles are precipitated from a solution containing no alkali ions.

Production of Ferrite from the FeOOH powder of Examples 5 and 6

To 500 g. of the γ-FeOOH and α-FeOOH powders obtained in Examples 5 and 6 were added highly pure $MnCO_3$ and ZnO powders containing less than 0.001% by weight of alkali irons in such a manner that a molar ratio of Fe_2O_3:MnO:ZnO=50.0:30.0:17.0 may result. The mixture was placed in a ball mill made of 18Ni—8Cr stainless steel; methyl alcohol was added; and the mixture was blended for 40 hours. The resulting slurry was filtered, dried, and ignited in air at 800°C for 4 hours. The mixture of oxides was press-moulded under pressure of 1.5 tons/cm^2, and the compressed product was kept at 1200°C for 4 hours in an atmosphere of N_2 containing 0.2% of O_2. The resultant sintered Mn-Zn ferrites, containing 0.036% of SiO_2 and 0.6% of CaO and having an average grain size of 1—2μ, had the following characteristics: μ_o at 100 kHz was 200—2150; and tan δ/μ_o was 1.9×10^{-6}.

In order that the Mn-Zn ferrites sintered at 1200°C should have μ_o at 100 kHz of more than 2000, it is preferable that the particle size of FeOOH, should be 0.5—2μ in width and more than 0.1μ in thickness and that the dimensional anisotropy should be small; for α-FeOOH particles, the width should be limited to 0.5—1.0μ. The reason for this is that if the particle size of the FeOOH precipitates is smaller, the particles tend to conglomerate during the drying operation, the mixing with the $MnCO_3$ and ZnO particles becomes non-uniform, and the rate of ferrite formation becomes lower.

WHAT WE CLAIM IS:—

1. A method of formation of iron oxyhydroxide particles in which substantially pure iron powder of particle size 140 microns or less is added to an aqueous solution of an acid, the pH of said solution being 3 or more, the concentration of said acid being at least 0.01 mole per litre and the amount of iron powder of particle size 40 microns or less being not more than 25 grams per litre of said solution, and an oxidizing gas is passed into said solution maintained at a temperature of 50°C to 70°C at a rate to maintain the iron powder in suspension until the iron powder dispersed in the solution disappears.

2. Method as claimed in claim 1 wherein the surface area of said iron powder is 0.3 m^2 per litre of said solution or more.

3. Method of formation of iron oxyhydroxide particles as claimed in claim 1 wherein said aqueous solution is an aqueous solution of at least one of sulphuric acid, hydrochloric acid, nitric acid and acetic acid, the concentration of the acid being 0.12 to 0.25 mol per litre.

4. Method as claimed in any preceding claim wherein said iron powder is a crushed electrolytic iron powder and said oxidizing gas is air.

5. Method as claimed in claim 4 wherein air is passed into the solution at a rate of 600 to 1500 litres per hour.

6. Method of formation of iron oxyhydroxide particles as claimed in claim 1 substantially as described with reference to the accompanying drawings.

7. Iron oxyhydroxide particles produced by the method claimed in any preceding claim.

8. A powder of iron oxyhydroxide as claimed in claim 7 in which the particles are elongated and are 0.3 microns or more in width and 0.1 microns or more in thickness.

9. Ferrites produced from iron oxyhydroxide as claimed in claim 7 or 8.

BUGNION & CO.,
110 Kennington Road,
London, S.E.11.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

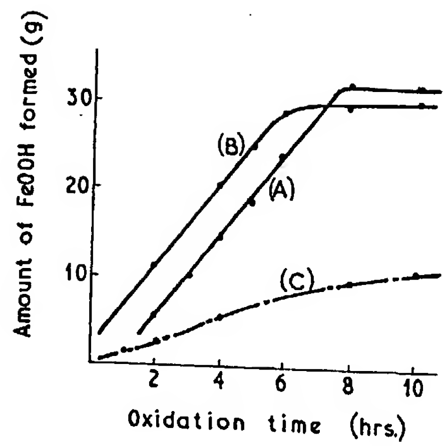
Amount of FeOOH formed (g)
30
20
10
(B)
(A)
(C)
2
4
6
8
10
Oxidation time (hrs.)

FIG. 1

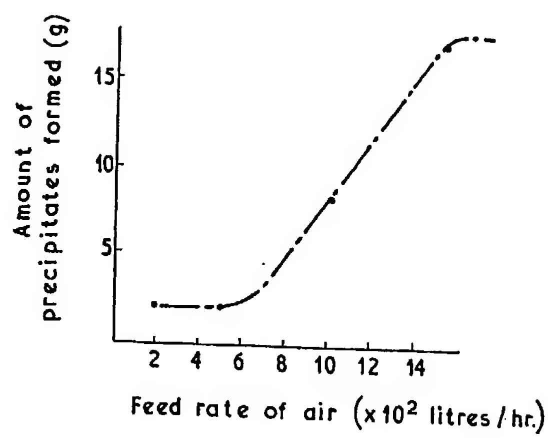
Amount of precipitates formed (g)
15
10
5
2
4
6
8
10
12
14
Feed rate of air (x 10² litres / hr.)

FIG. 2

1226876 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

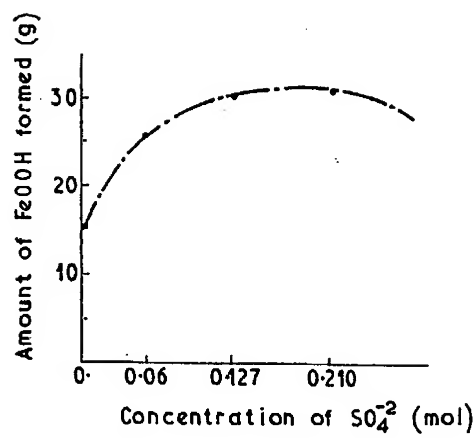

FIG. 3

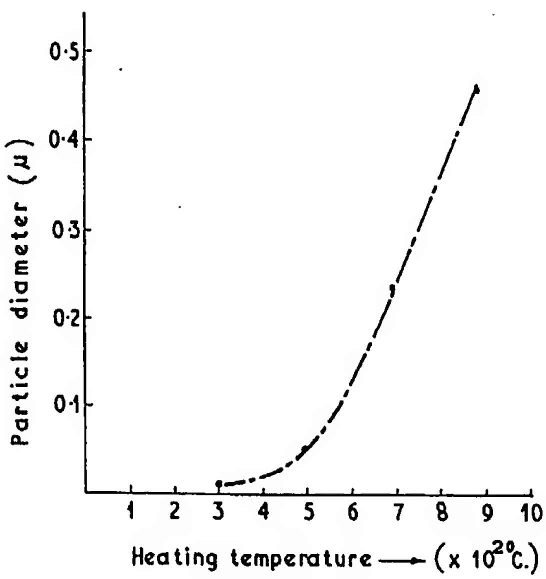

FIG. 6

1226876 COMPLETE SPECIFICATION
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 3

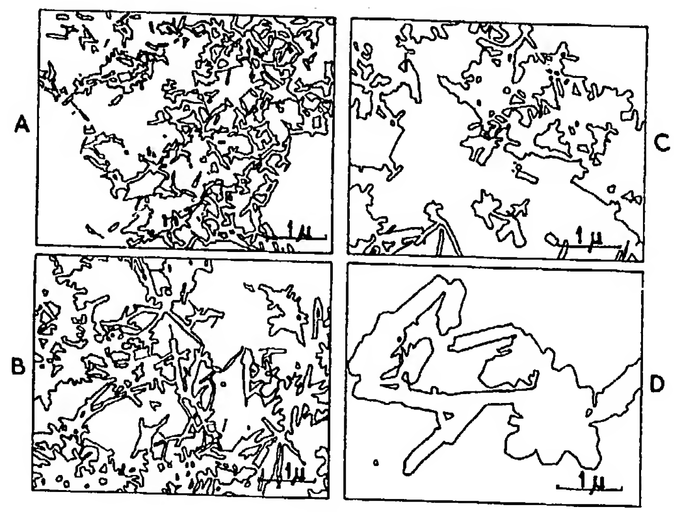

FIG. 4
Particle shapes of α-FeOOH

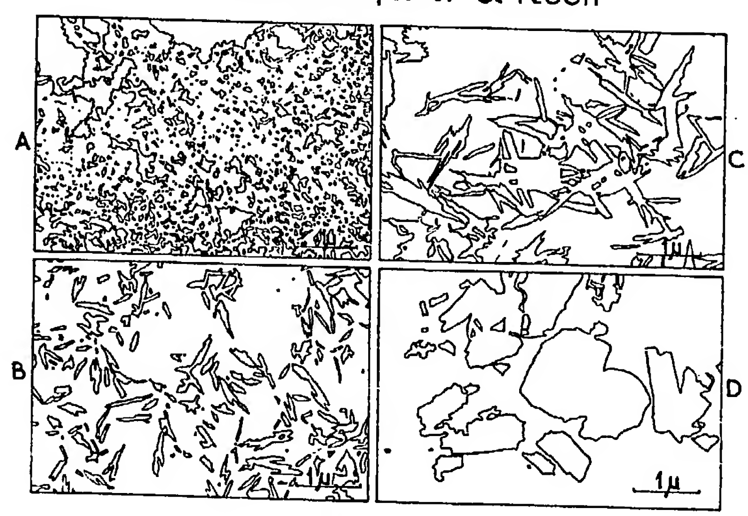

FIG. 5
Particle shapes of α-FeOOH